The reexamination of Pasteur's experiment in Japan

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An article written in Japanese in 1979 recorded the reexamination of the Pasteur's experiment on spontaneous resolution and many useful sketches of the hemihedral crystals of sodium ammonium tartrate.

This communication is a summary of an article written in Japanese in *Kagaku no Ryoiki*, 1979, **33**, 951–962 by Professor Masao Nakazaki entitled 'Morphology of sodium ammonium tartrate: Pasteur's spontaneous resolution and its reexamination,'[1] and this was written with consent of the author and the publisher, Nankodo, Co. I wish to introduce the article on this occasion with a hope that it would help our understanding the real morphology of Pasteur's crystals.

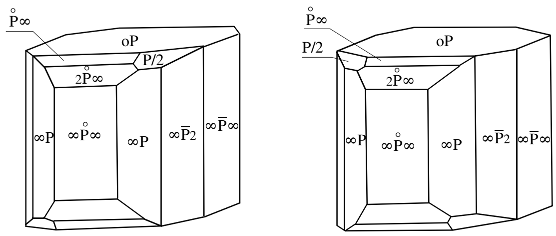

Figure 1 Sketches of the hemihedral crystals of sodium ammonium tartrate according to Kekulé.

Professor Nakazaki's motivation to write the article recording his own results is the following: first, many textbooks of organic chemistry and stereochemistry cited the hemihedral crystal models shown in Figures 1[2] and 2[3] as that of the Pasteur's salt. However, not only because these look different but also because the real crystals were reported by Pasteur to be more complex than the simplified model shown in Figure 2, it is natural

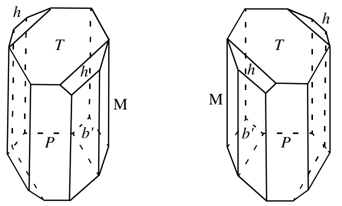

Figure 2 Simplified form of hemihedral crystals of sodium ammonium tartrate according to Pasteur.

to ask 'How did the Pasteur's crystals look like?' Although there are several reports on the reexamination of the Pasteur's experiment,[4] there is no sketch of the crystals nor the pictures which were clear enough to understsand their morphology. Moreover, in some textbooks, there are descriptions such as 'Pasteur separated the crystals mechanically with tweezers using a microscope (or a loupe),' but he did not seem to tell anything about it. Are the crystals too small (or too complicated) to be identified by naked eyes? Are they hard enough to be picked up by tweezers? In addition, there seemed to be a slight difference in the experimental observations between that of the Nakazaki's group and the others.[4] In order to clarify these issues, he decided to reexamine the experiment with his extremely skilled collaborator Dr. Yoshiki Hirose.

The article starts with a brief summary of the historical background of the Pasteur's experiment and the argument regarding the crystal form of sodium ammonium tartrate. It is followed by the experimental procedure for the preparation of the crystals (spontaneous resolution), mechanical separation, and the morphology of the hemihedral crystals, as well as that of the holohedral crystals of the racemate salt. It ends with a comment on the stereochemical term 'dissymmetry' and the D,L designation of the configuration of tartaric acid. This communication focuses on the central part of the article.

Figure 3 Large crystals of sodium ammonium tartrate prepared by the seeding method. Left, (–)-enantiomer; right, (+)-enantiomer: the pictures are taken for the crystals prepared about 25 years ago and stored as described in the text.

Experimental procedure.

In a 200 ml beaker containing 50 ml of water 15 g of a racemic acid was dissolved with warming. Anhydrous sodium carbonate was added in small portions with swirling (Caution: effervescence). Although an acidic salt may precipitate during the addition, it dissolved after all sodium carbonate was added. To this solution another 15 g of the racemic acid was added. While all the acid did not dissolve, 30 ml of concentrated aqueous ammonia (28%) was added in portions with swirling. Exothermic reaction took place and the acid dissolved when *ca*. 22 ml of ammonia was added. After all ammonia was added, the viscous solution was decanted to a 200 ml beaker to remove any small piece of the solid material present, if any, at the bottom of the beaker, which would result in irregular crystal formation. The beaker was allowed to stand at 25 °C without a cover to evaporate ammonia and water slowly. To supplement the evaporated ammonia, 0.5–1.0 ml of concentrated ammonia was added once every two days. Depending on the temperature and moisture, crystals of 7–10 mm appeared after 3–5 days. Leaving the solution longer in attempts to grow larger crystals resulted in interlacement of the crystals, which were difficult to separate without breaking.

The supernatant solution was decanted slowly to a 200 ml beaker, 0.5 ml of conc. NH_3 was added, and the solution was allowed to stand to give the second crops. The crystals in the beaker were picked up with fingers and blotted with a tissue paper. Typically, 6–7 g of crystals were obtained. Use of tweezers stimulates the crystallization on the wet surface of the crystals, resulting in the formation of very small powdery crystals on the surface.

However, the experiment was rarely successful. In most cases, crystals did not appear after standing long. In such a case, it was better to scratch the wall of the beaker with a glass bar to force deposition. Then the supernatant solution was decanted and the remaining crystals were dissolved with a minimum amount of water at room temperature. The decanted solution was put back, the combined solution was warmed to 50 °C, and a small amount of conc. ammonia was added before allowing it to stand

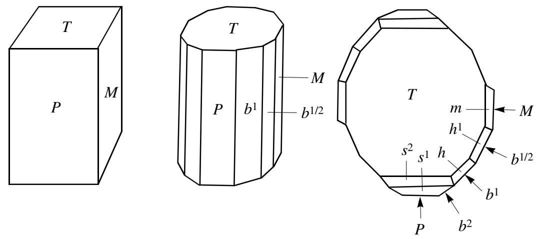

Figure 4 Sketches of a hemihedral crystal of sodium ammonium tartrate according to Pasteur.

at room temperature. The solutions thus prepared had a better chance of forming good crystals. Many trials and errors should be done to get experienced, and a keen scent was necessary for getting good crystals. However, it was not sure whether they became skilled or the laboratory was polluted with (invisible) seed crystals after many experiments.

Mechanical separation.

Since most of the crystals were interlaced, only less than half of them were separated mechanically by identifying the direction (right or left) of the *h* plane relative to the T–s^2–s^1–P planes of Figure 5 shown later. The specific rotations ($[\alpha]_D^{25}$) of a number of right and left hemihedral crystals were recorded in H_2O (*c* 0.86–2.04), which ranged from +21.1 to +22.7 and from –21.9 to –24.3, respectively. Typically, 0.1–0.3 g each of enantiomeric crystals were obtained, with (+)-enantiomer slightly more than (–)-antipode. The reason for this uneven distribution, which was also described in the literature,[4] was not clarified. The crystals were large enough to be identified by naked eyes without the use of a microscope or a loupe.

For demonstration purposes, large crystals (15–25 mm) were grown by a simplified modification of the seeding method.[5] Thus, small crystals (*ca*. 5 mm) with sharp edges were tied by a fishing gut and dipped in the above racemic acid solution near the bottom of the beaker and the solution was allowed to stand below 25 °C. The large (15–25 mm × 8–10 mm) transparent crystals thus obtained (Figure 3) had a tendency to lose luster in air probably by losing the crystal water. The crystals also tended to crumble easily that it was not possible to use tweezers. They were best kept in a soft container like a sealed polyethylene bag rather than a vial.

Morphology of the crystals.

In the Pasteur's literature,[1,6] the illustrations shown in Figure 4 were given. Professor Nakazaki was not able to observe the b^2 plane probably because this plane is too small. By ignoring this plane, 'ideal' hemihedral crystals possessing D_2 symmetry with all planes developed adequately were drawn as in Figure 5. Its wooden models were also made (Figure 6).

Figure 7 gives sketches of six different crystals from the top and bottom faces of the (+)-antipode. Figure 8 represents detailed sketches from the top and four side views of a (+) crystal. These sketches were made for the relatively large (*ca.* 15 mm × *ca.* 10 mm) crystals obtained by the seeding method. As shown in Figures 7 and 8, the real crystals were substantially deformed from the 'ideal' shape (Figures 5 and 6). However, a closer inspection revealed that every crystal possessed eaves plane *h* at either right side of the T–s^2–s^1–P plane (dextrorotary) or the left side of it (levorotary). These illustrations showed clearly the forms of the Pasteur's crystals, which had not been visualised in such

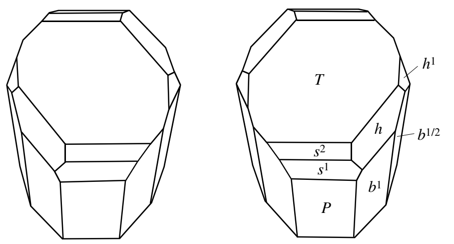

Figure 5 'Ideal' hemihedral crystals of sodium ammonium tartrate.

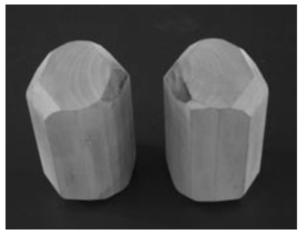

Figure 6 Wooden models of the 'ideal' hemihedral crystals of sodium ammonium tartrate.

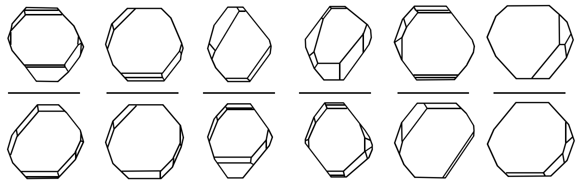

Figure 7 Sketches of six different hemihedral crystals of sodium ammonium tartrate.

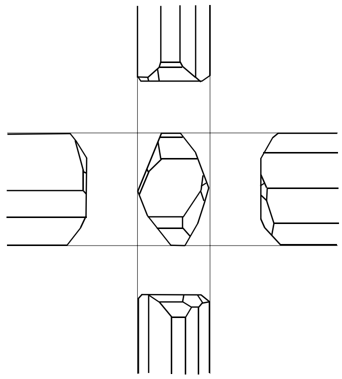

Figure 8 Sketches of a hemihedral crystal of sodium ammonium tartrate viewed from different directions.

unambiguous forms for a long time. Professor Nakazaki also prepared the holohedral crystals of sodium ammonium racemate, the crystal form of which had been only imperfectly drawn.[4,7]

The author is grateful to Professor Y. Hirose, a former collaborator of Professor Nakazaki, for the pictures of the crystals and the wooden crystal models.

References and Notes

1 M. Nakazaki, *Kagaku no Ryoiki*, 1979, **33**, 951 (in Japanese).

2 According to the Nakazaki's article,[1] the sketch in Figure 1 originates from Kekulé's *Lehrbuch der Organischen Chemie*, Vol. II as pointed out by Lowry: T. M. Lowry, *Optical Rotatory Power*, Longman, Green & Co., London, 1935.

3 The sketch in Figure 2 was taken from the Pasteur's original paper: L. Pasteur, *Ann. Chim. Phys*., 1850, **28** (3), 56. However, at the same time, Pasteur pointed out that the actual form of the crystals was more complex than that shown in Figure 2.

4 (*a*) G. B. Kauffman and R. D. Myers, *J. Chem. Educ*., 1975, **52**, 777; (*b*) M. Miyake, *Kagaku Kyoiku*, 1977, **25**, 325 (in Japanese).

5 T. S. Patterson and C. Buchanan, *Ann. Sci*., 1945, **5**, 288.

6 L. Pasteur, *Ann. Chim. Phys*., 1848, **24** (3), 442.

7 A. Scacchi, *Rend. Accad. Sci. Fis. Mat. Napoli*, 1865, **4**, 250.

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